



PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

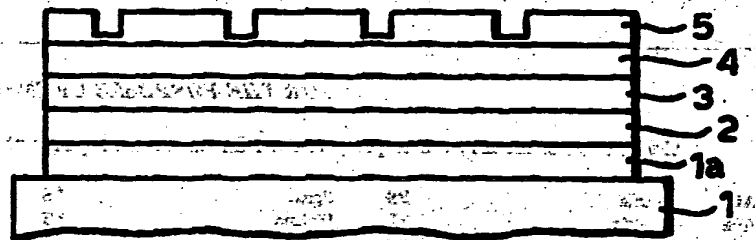
INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : H01L 51/20, 27/15		A1	(11) International Publication Number: WO 98/53510
			(43) International Publication Date: 26 November 1998 (26.11.98)
(21) International Application Number: PCT/GB98/01265		(81) Designated States: JP, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).	
(22) International Filing Date: 30 April 1998 (30.04.98)			
(30) Priority Data: 9710344.4 21 May 1997 (21.05.97) GB		Published <i>With international search report.</i>	
(71) Applicant (for all designated States except US): CAMBRIDGE DISPLAY TECHNOLOGY LTD. [GB/GB]; 181A Huntingdon Road, Cambridge CB3 0DJ (GB).			
(72) Inventors; and (75) Inventors/Applicants (for US only): PICHLER, Karl [AT/GB]; 3 Victoria Park, Cambridge CB4 3EJ (GB). BRIGHT, Christopher [GB/GB]; 3 Van Gogh Place, St. Ives, Huntingdon, Cambs. PE17 6HE (GB).			
(74) Agents: SLINGSBY, Philip, Roy et al.; Page White & Farrer, 54 Doughty Street, London WC1N 2LS (GB).			

(54) Title: PATTERNING ORGANIC LIGHT-EMITTING DEVICES

(57) Abstract

A method for patterning an organic light-emitting device having an organic light-emitting layer underlying an electrode layer, the method comprising: a first patterning step, in which the electrode layer is patterned by exposure to a laser beam so as to remove part of the depth of the electrode layer in the areas patterned by the laser beam; and a second patterning step in which the remaining depth of the electrode layer is removed in the areas patterned during the first step, the second patterning step being of a type to which the organic layer is less sensitive than that of the first patterning step.



FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front-pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

PATTERNING ORGANIC LIGHT-EMITTING DEVICES

This invention relates to methods for patterning organic light-emitting devices ("OLEDs"), and to patterned organic light-emitting devices themselves.

One type of organic light-emitting device is described in PCT/WO90/13148, the contents of which are incorporated herein by reference. The basic structure of this device is an electroluminescent polymer film (for instance a film of a poly(p-phenylenevinylene) - "PPV") sandwiched between two electrodes, one of which injects electrons and the other of which injects holes. It is believed that the electrons and holes excite the polymer film, emitting photons. These devices have potential as flat panel displays, in which case one of the electrodes is transparent; for example made of indium-tin oxide ("ITO").

Another type of organic light-emitting device is a small molecule device, details of which are given in US 4,539,507, the contents of which are incorporated herein by reference. In these the light-emitting layer is of a small molecule material, such as tris(8-hydroxyquinoline)aluminium ("Alq₃"), sandwiched between the two electrodes.

To manufacture patterned organic display devices, for example pixellated monochrome or multi-colour display devices, or other organic light-emitting devices (e.g. print heads) having several distinct light-emitting regions, there is a need to pattern one or more layers of the device. Typically, in a matrix display device, having pixels arranged in rows and columns, the organic layer(s) sandwiched between the anode and the cathode are of the order of 100nm thick. The separation from row to row or column to column of the matrix is, even in a very high-resolution display, of the order of several microns but typically much more. This, together with the typically low intrinsic conductivity of semiconductive electroluminescent molecular or polymeric materials helps

prevent current spreading along the organic layer(s) and therefore current leakage or shorting between rows or between columns via the organic layer(s).

During the patterning process there is a great risk of exposing sensitive layers and interfaces of the OLED stack to substances or processes which can cause degradation in device performance, e.g. ambient gases and moisture, photoresist solutions, developer solutions for photo-resists, solvents, exposure to UV light or plasma treatment. It has been observed that the exclusion of moisture from OLEDs is of paramount importance to achieve good device performance and in particular good device operating and shelf lifetime. This issue is of particular concern during patterning of the cathode, which is typically of a reactive and moisture sensitive metal or alloy.

Typically, one of the electrodes (the "bottom electrode") is deposited on a substrate (e.g. a glass sheet) before the organic layer is applied. The bottom electrode is easily patterned by, for instance, standard photolithographic techniques.

The "top electrode" is generally deposited on to the organic layer. Therefore, patterning the top electrode is more difficult. One solution is to deposit the top electrode through a shadow mask. However, the shadow mask technique cannot generally provide the fine resolution patterning needed for high-density patterning. Another solution is to use photolithographic etch or lift-off techniques. However, this is an elaborate process which adds considerable complexity to the production system, and the chemicals involved can cause contamination of the layers of the device. In order to achieve good performance in OLEDs it is of great importance to optimise all the individual layers: the anode, the cathode and the organic layer(s), as well as the interfaces between the layers. Ingress of moisture or solvents into the organic layer(s), the electrodes, particularly the cathode, and the interfaces can be extremely detrimental to the device performance and especially to the operating and shelf life.

EP 0 758 192 A2; "Microfabrication of an Electroluminescent Polymer Light Emitting Diode Pixel Array", Noach et al., Appl. Phys. Lett. 69, 3650 (1996); "Microfabrication of an Electroluminescent Polymer Light Emitting Diode Pixel Array", Faraggi et al., Synth. Met. 85 (1997) 1187 and JP 8-222371 describe methods for patterning the top electrode of a device by laser scribing. Laser scribing has the advantage that it allows high-resolution patterning: the minimum laser spot size can be well below 50 μm . However, none of these documents addresses the problem that in an organic light-emitting device, because the organic layer underlying the top electrode is so sensitive it is easily destroyed by the laser beam as soon as the top electrode has been removed by the laser scribing. This is particularly so because the top electrode layer is typically of a material that is highly reflective, and therefore requires a relatively high laser power for its erosion. Another risk is that the organic layer may not absorb the laser radiation. Then, as soon as the top electrode is scribed through, the laser light is transmitted through the organic layer to the bottom electrode. This can cause great damage to the device as the bottom electrode is ablated whilst sealed between the substrate and the organic layer.

According to a first aspect of the present invention there is provided a method for patterning an organic light-emitting device having an organic light-emitting layer underlying an electrode layer, the method comprising: a first patterning step, in which the electrode layer is patterned by exposure to a laser beam so as to remove part of the depth of the electrode layer in the areas patterned by the laser beam; and a second patterning step in which the remaining depth of the electrode layer is removed in the areas patterned during the first step, the second patterning step being of a type to which the organic layer is less sensitive than to that of the first patterning step.

Thus, the first step may be sufficiently intense to allow for rapid removal of a part of the electrode layer, whilst the removal of the final thickness of the electrode layer may be performed with reduced risk of damage to the organic

layer. The invention thus provides particular advantages when the first patterning step is of an intensity sufficiently high to erode substantially material of the type comprised in the organic light-emitting layer. Furthermore, since the organic layer is relatively insensitive to the second patterning step it may protect underlying layers (which may be more sensitive to the type of patterning of the second patterning step) from damage.

The intensity of the first patterning step is suitably sufficiently high to erode material of the type comprised in the organic light-emitting layer. The intensity of the second patterning step is suitably less aggressive in its removal of material of the type comprised in the organic light-emitting layer than the first patterning step. Preferably the intensity of the second patterning step is not sufficiently high to erode substantially material of the type comprised in the organic light-emitting layer. Preferably the second patterning step is of a type that does not significantly erode the organic light-emitting layer, or erodes that layer only weakly and/or gradually and/or controllably; one example of such a type may be reactive ion etching.

The first patterning step is preferably a laser scribing step. The laser used for the first step is suitably an ultraviolet, visible or infra-red laser.

In the second patterning step too, the electrode layer may suitably be patterned by a laser beam. The parameters for the laser operation during the second patterning step are suitably chosen so that the scribing effect of the beam is less than in the first step. For example, it is preferred that the incident power of the laser (i.e. the power incident on a unit area in unit time) is less intense for the second patterning step than for the first. The laser used for the second patterning step is suitably an infra-red (e.g. ND-YAG), visible or ultraviolet (e.g. excimer) laser.

In the second step the electrode layer may be patterned by etching, most preferably dry etching (e.g. plasma etching, in particular reactive ion etching, and preferably anisotropic reactive ion etching).

The first patterning step preferably removes from 50% to 95% of the thickness of the electrode layer in the areas that are patterned, most preferably around 80%. After the first patterning step there is preferably a sufficient amount of material remaining in the areas that are patterned that the remaining material is opaque to the laser radiation; for instance, the remaining material is preferably at least 10nm thick. This remaining material may be regarded as a laser barrier left after the first patterning step. The second patterning step preferably removes the remaining thickness of the electrode (i.e. the barrier) in the areas that are patterned in the first step.

The electrode layer may suitably comprise an electrically conductive layer and a layer of protection material on the face of the conductive layer opposite the light-emitting layer. The electrode layer may suitably comprise an electrically conductive layer and a layer of laser absorbing material on the face of the conductive layer opposite the light-emitting layer. In either case, it is preferred that during the first patterning step the electrically conductive layer is not substantially patterned.

Preferably the or each laser beam is applied in pulses. The pulses suitably have lengths of less than 1ns, most preferably less than 10ps.

The electrode layer may be a cathode or an anode. The electrode layer, or at least the conductive part of it, or the portion of the electrode layer at its face closest to the light-emitting layer suitably has a work function less than 3.5eV if a cathode or greater than 4.0eV if an anode. The electrode layer may be transparent or semi-transparent, at least at the frequency of emissions from the organic light-emitting layer.

The light-emitting layer is suitably a light-emitting polymer layer, preferably a light-emitting conjugated polymer layer. The organic material of the light-emitting layer may be a soluble material and/or a solvent-based material. The material may be a luminescent material. The material is preferably a conjugated or partially conjugated material, most preferably a conjugated polymer material. The material preferably comprises an electroluminescent polymer, such as PPV, poly(2-methoxy-5(2'-ethyl)hexyloxyphenylene-vinylene) ("MEH-PPV"), a PPV-derivative (e.g. a di-alkoxy or di-alkyl derivative), polyfluorenes, polyparaphenylenes, polythiophenes, etc. or copolymers thereof and including substituted and/or unsubstituted versions thereof. The material may comprise a luminescent organometallic polymer. The material may comprise a small molecule luminescent material such as (Alq₃).

In another method, the areas of the electrode layer patterned in the first step could, rather than being removed, rendered insulative – for instance by oxidation. That method thus comprises a first, higher intensity patterning step, in which the electrode layer is patterned by exposure to a relatively high intensity laser beam; and a second, lower intensity patterning step, in which the electrode layer is rendered insulative in areas patterned during the first step.

According to a second aspect of the invention there is provided a method for forming an organic light-emitting device on a substrate, comprising the steps of: depositing a first layer of a conductive organic material on the substrate; depositing a second layer of a light-emitting organic material on the first layer; and patterning the second layer by exposing it to a laser beam of a frequency that is substantially absorbed by the conductive organic material and substantially absorbed by the light-emitting organic material.

The conductive organic material is suitably a polyaniline, polypyrrole or polythiophene derivative, e.g. polystyrene sulphonic acid doped polyethylene dioxythiophene.

Suitable materials and classes of materials for the first light-emitting material include those set out above in relation to the organic light-emitting layer of the first aspect of the invention.

The substrate may suitably include an electrode layer. Suitable electrode materials and classes of materials include those set out above in relation to the electrodes of the first aspect of the invention.

The second aspect of the invention may provide a method for forming a multi-colour organic light-emitting device. To provide such a device the method preferably comprises, following the patterning step, further steps of: depositing a third layer of a conductive organic material on the second layer; depositing on the third layer a fourth layer of a second light-emitting organic material; and patterning the fourth layer by exposing it to a laser beam of a frequency that is substantially absorbed by the material of the third layer and substantially absorbed by the second light-emitting organic material; the second light-emitting material having a different spectrum of light emission from that of the first light-emitting material. Similar additional steps may be repeated to deposit further layers of other light-emitting materials. Most preferably three such layers are deposited. Suitable colours for the emissions from the layers are red, green and blue.

The conductive organic material of the third layer (and any subsequent layers of conductive organic material) is suitably the same as the material of the first layer. The conductive organic material of such a third layer is suitably polystyrene sulphonic acid doped polyethylene dioxythiophene.

Suitable materials and classes of materials for the second light-emitting material (and any subsequent light-emitting materials) include those set out above in relation to the organic light-emitting layer of the first aspect of the invention.

According to the present invention from a third aspect there is provided a method for patterning an organic light-emitting device having a first electrode layer, a second electrode layer and an organic light-emitting layer located between the electrode layers, the method comprising patterning the first electrode layer by exposing it to a laser beam of a wavelength that is absorbed by the organic light-emitting layer so that the organic light-emitting layer serves to protect the second electrode layer from patterning by the laser beam. The laser wavelength is suitably chosen such that it is within the absorption band of the organic layer. Suitable materials and classes of materials for the layers of the device include those set out above in relation to the first aspect of the invention.

The present invention also provides an organic light-emitting device manufactured by the methods of the first, second or third aspects of the invention.

Any orientations referred to or implied or inferred above reflect only the mutual arrangement of the components of the device and not any absolute orientation of the device during manufacture or use.

The present invention will now be described by way of example with reference to the accompanying drawings, in which:

figure 1 shows a cross-section of part of an organic light-emitting device on the line A-A of figure 2;

figure 2 shows a plan view of the whole device of figure 1 before patterning;

figure 3 shows a plan view of the whole device of figure 1 after patterning;

figure 4 shows a cross section of a device of the type shown in figure 1 after a first patterning step;

figure 5 shows the device of figure 4 after a second patterning step;

figure 6 shows a cross-section of a first alternative device after a first patterning step;

figure 7 shows a cross-section of a second alternative device after a first patterning step;

figure 8 shows a cross-section of the device of figure 7 after a second patterning step; and

figures 9 to 12 show steps in the production of a third alternative device. The figures are not to scale.

The device of figure 1 has a glass sheet 1 which carries an anode layer 2 for injecting positive charge carriers, a first organic layer 3, a second organic layer 4 and a cathode 5 for injecting negative charge carriers. The anode layer is formed of indium-tin oxide ("ITO"). The first organic layer is formed of polystyrene sulphonic acid doped polyethylene dioxythiophene ("PEDT/PSS"). The second organic layer is formed of PPV. The cathode is formed of an alloy principally of aluminium and lithium. The device uses PPV as the light-emitting layer. The device is encapsulated in glass epoxy (not shown).

The manufacture of the device will now be described. The glass substrate is a polished glass sheet of sodalime glass 1.1mm thick, with a barrier layer 1a of silicon dioxide around 100nm thick on its upper surface. The ITO anode is deposited on to the silicon dioxide by a conventional DC or RF sputtering technique. The completed ITO layer is about 1500Å thick with a sheet resistance of around 15 Ohm/square and a transparency of about 85%. Alternatives to ITO are other conductive materials such as fluorine-doped tin-oxide, aluminium-doped zinc-oxide, metals such as gold, alloys and conductive polymers such as polystyrene sulphonate-doped polyethylene dioxythiophene (PEDT/PSS) or doped polyaniline, or combinations thereof. To provide an effective anode the material is preferably a high work function material, with a work function higher than, say, 4.0 or 4.5eV. In devices like the one of figure 1, where the emitted light is to be transmitted through the anode, the anode should be at least partially transparent.

At this stage the ITO layer can, if necessary, be patterned, for example by conventional wet-chemical ITO patterning techniques, and then cleaned.

The PEDT/PSS is a conductive polymer layer. The PEDT/PSS mixture is prepared (see EP 0 686 662 and Bayer AG's Provisional Product Information Sheet for Trial Product AI 4071), deposited on to the ITO layer by spin coating and then heated for 1 hour at 110°C in a nitrogen atmosphere. The thickness of the completed PEDT/PSS layer is around 500Å. The PEDT/PSS layer could be omitted provided the resulting device had the required stability and current/voltage performance.

The PPV is then deposited over the PEDT/PSS layer. A precursor polymer, typically a precursor to a homopolymer PPV with a tetrahydrothiophene leaving group (attached to the ethylenic group) or a copolymer containing in addition non-leaving acetate groups (attached to the ethylenic group) is deposited on to the PEDT/PSS from solution by spin-coating. This is then converted at 150°C in high purity nitrogen for four hours. The solubilising group that is removed during conversion is tetrahydrothiophene and the counter ion to the thiophenium salt is bromide. The completed PPV film is around 1000Å thick. Instead of a polymer layer, the organic light-emitting layer could be of a small molecule material such as Alq₃.

The cathode is an aluminium alloy containing around 95% Al with 2.5% Li, 1.5% Cu, 1% Mg and 0.1% Zr (all by weight). The cathode is DC magnetron sputtered on to the organic PPV layer to a thickness of 1200Å. The cathode could be made of other metals or alloys with low work functions, for instance Ca, Ba, Yb, Sm, Li or alloys of such elements with Ag, Al etc, such as Mg:Ag, Mg:In or other Al alloys. To provide an effective cathode the material is preferably one having a low work function, e.g. less than 3.0eV or 3.5eV. At the edges of the device the cathode sputtering is masked, and the organic

layers are not deposited, so as to allow for contacts to be fixed to the top surface of the anode (as illustrated at the left of figure 2).

At this stage, as shown in figure 2, the cathode 5 extends in an integral block across the device. If a voltage is applied between the anode 2 and the cathode 5 light is emitted from the entire area of the PPV layer 4 lying between the block of the cathodes and the anode 2. However, if the device is to be used in an application where the light-emitting layer is to have distinct, individually controllable regions (e.g. a pixellated display or a print head) at least one of the layers of the device must be patterned.

The patterning methods described below make use of laser scribing/ablation to provide high-resolution patterning. The laser scribing/ablation system is an HK Technology HKR-2 laser scribing station as, for example, supplied by Hahn & Kolb GB Ltd. of Rugby, United Kingdom, utilising a 25W Q-switched CW YAG laser. A computer-controlled galvo-mirror system is used to direct the beam relative to the device in order to perform the laser patterning. Some specific scribing parameters will be set out below, but in general the pattern definition technique and precise method and parameters of the laser scribing/ablation process should be chosen in accordance with the OLED device structure that is being patterned: in particular the thicknesses and material parameters of the specific layer(s) to be laser-patterned. The main parameters defining the laser scribing/ablation process are: laser wavelength, laser power, DC versus pulsed operation, pulse duration, pulse duty cycle and/or frequency, spot size, scan speed, single versus multiple pass/exposure to define a scribed line, scanning of the laser (focused onto the device versus patterning of the laser through a mask) and scribing/ablating in vacuum, air, inert or chemically reactive atmosphere. An overview of such laser processing techniques and guidelines for the choice of parameters depending on the application and the materials to be scribed/ablated can, for example, be found in D. Bäuerle, Laser Processing and Chemistry, second edition, Springer (Berlin, Heidelberg), 1996.

The patterning methods described below relate to the patterning of the device to provide a series of individual linear light-emitting regions (20 in figure 3) separated by linear non-emitting regions (21 in figure 3). A device of this type is suitable as a print head or a device emitting in rows which is useful as a sequentially addressed backlight for LCDs. (Emitting and non-emitting regions of any other desired shape could be provided). To provide the linear patterning the laser beam is arranged to scan the cathode in a linear motion to define a non-emitting region as will be described below. After one or more of these linear scans the beam is tracked perpendicular to the scan direction so as to allow the next non-emitting region to be defined by the next scan(s).

In a first patterning method each non-emitting region is defined in a single pass of the beam. The intensity of the beam (as set by parameters such as the beam power, spot size and the tracking speed relative to the device) is set so that the beam scores a linear groove into the cathode as it scans across it. The parameters are set such that the groove is not of the full depth of the cathode; in other words, even in the area scanned by the beam not all the material of the cathode is removed. The depth of the groove is suitably around 80% of the cathode thickness, leaving around 20% of the cathode thickness at the base of the groove. By choosing other scribing parameters (e.g. lowering the power) the groove could be cut by more than one scan of the beam.

After a groove has been cut to the desired depth, the beam is moved perpendicular to the groove direction to cut another parallel groove spaced from the first one (as illustrated in cross section by figure 4). In this specific embodiment the pitch of the line array (i.e. the distance from one emitting line to the next) is 1mm and the laser scribed/ablated gaps between the emitting lines are about 110 μ m wide. Laser scribing is a useful technique for this fine scribing operation because of the precise definition it provides.

Once all the necessary grooves have been scribed the cathode is etched using a dry etch process. This erodes the cathode over its full surface to remove the

cathode completely in the thinned areas. The parameters of the dry etch process (e.g. the etch time and etchant concentration) are chosen to give good control over removing the thickness of the thinned areas. Suitable parameters for the etching process for an Al:Li alloy are: a reactive ion etch system using an SVS research machine, the etch gas being SiCl_4 at a pressure of 40 mTorr and roughly 30 sccm gas flow, a peak voltage of 500V, a bias voltage of 245V, resulting in an etch rate of around 300Å/minute. After the thinned cathode areas have been removed the whole surface is passivated in the reactive ion etch machine using CF_4 gas.

This two-stage patterning procedure has a number of advantages. First, it allows the laser scribing operation to be used to define precisely and to a high resolution the areas of the cathode to be removed, reducing risk of damaging the sensitive organic layer 4 by exposing it to laser light. The etch process tends not to cause sudden erosion of the cathode, as can occur in a basic laser scribing operation, because the cathode is protected by the organic layer from the etch. The etching process is also more controllable for the fine removal of the last parts of the cathode than laser scribing. And the use of a dry process for the etching step helps reduce the risk of chemical contamination of the layers of the device during the etch. Aluminium oxide, aluminium nitride, silicon oxide etc. to serve as insulating layers can be deposited in the same chamber.

It should also be noted that the remaining metal, after laser scribing, helps to protect the organic material from the environment.

The cathode is typically relatively reflective to the laser beam. For instance, aluminium has a reflection coefficient of around 0.9 at a typical excimer laser wavelength of 248nm or a typical Nd-YAD laser wavelength of 1064nm. Therefore, before the scribing step it may be found advantageous to provide the cathode, over its upper surface, with a layer 6 (see figure 6) of a material that has a lower reflection coefficient than the cathode at the frequency of the laser. Examples are carbon (graphite), a non-stoichiometric oxide (for example

oxygen deficient aluminium-oxide, which tends to be brown) or zirconium, which has a reflection coefficient of only around 0.015 at 248nm and 0.14 at 1064nm. Then the device is scribed (as described above) through the layer 6 and then etched as described above. In this method, the laser absorbent layer 6 helps initiate laser erosion of the cathode, allowing a lower intensity of scribing (e.g. a lower laser power) to be used, and increasing control over the depth to which the cathode is scribed.

Another option is, before the scribing step, to provide the cathode over its upper surface with a mask layer 7 of a material that is resistant to the dry etch process. Then during the scribing step the etch-resistant layer 7 is scribed so as to remove the layer 7 over the areas where the cathode is to be removed (see figure 7). The control of the laser parameters for this step can be somewhat loose because it does not matter if some of the underlying cathode is also removed at this stage. Then the etch step is carried out to remove the areas of the cathode that are not protected by the etch mask (see figure 8). The layer 7 could be a photo-resist or an organic layer which is easily laser scribed but can serve to protect the cathode during the etch process.

The quality of the final device can be improved considerably if steps are taken to minimise the amount of reactive particles that are present during the scribing operation. Because the scribing operation exposes parts of the cathode there is a risk that these parts may react, impairing the performance of the device. This is especially important when areas of the cathode that are to form the edges of light-emitting regions are exposed. One way of reducing the amount of reactive particles present is to perform the laser scribing/ablation process in an atmosphere that contains no or only negligible amounts of chemical species that may chemically react with the cathode. Thus the scribing may be performed in a vacuum or an inert atmosphere such as, for example, dry nitrogen or argon, to prevent or at least minimise the exposure of the OLED to air and in particular moisture. Another useful step is to minimise exposure of the cathode even before the scribing operation. One option is to cover the

cathode with a protective layer of a material such as silicon-nitride, aluminium-oxide, silicon-oxide or a conformal organic material such as Parylene (available from NovaTran™) or doubling as absorbing layer 6 or etch resistant layer 7. Another option is to deposit the cathode and then control the atmosphere to which it is exposed before the scribing operation. This may be done by making use of load locks linking the laser scribing apparatus with the other pieces of OLED fabrication and/or storage equipment.

Another way to protect the cathode is to cover it with a protective layer of an inorganic material, for example of aluminium-oxide, silicon-oxide or silicon nitride, which is insensitive to the etch process that is to be used. Then the cathode and its protective layer can be patterned by, for instance, laser scribing to remove at least the protective layer over the areas of the cathode that are to be patterned. The laser scribing step could be of any suitable type, including multi-pass. Then, when the etch process takes place the areas of protective layer that are left protect their underlying areas of the cathode from removal, but where the protective layer has been removed any thickness of the cathode that remains can be removed by the etch process.

Laser scribing can generate significant heat in the device. Therefore, it is useful to pulse the scribing laser to allow time for heat to dissipate between pulses. As an example, the length of the pulses can suitably be around or less than 10ps, with a gap between pulses of around 1 to 10 ms.

Suitable options for the dry etch process are reactive ion etching (particularly anisotropic ion etching) and plasma etching. An alternative to removing the thinned portions of the cathode is to render them non-conductive, for example by oxidising them under bombardment by oxygen gas (or implantation). In the latter case, a protective layer over the non-thinned portions of the cathode may be used to protect them from oxidation, in an analogous manner to the etch mask process of figures 7 and 8.

Another alternative to etching is to perform the second stage of the patterning process using a relatively low power laser scribing technique. For instance, in a first pass of the laser beam at high power (using the parameters such as those listed above) 80% of the thickness of the cathode may be removed, forming a groove in the cathode. Then the laser beam may be reduced to lower power and tracked one or more times over the groove to remove the remaining 20% of the cathode. Because the final removal of the cathode is performed at relatively low power, the potential damage to the organic layer and the anode is reduced.

Either of the laser scribing steps may be performed as a laser-assisted etching step. In laser-assisted etching the scribing is performed in an atmosphere which is capable of aiding the scribing process. For example, a pure aluminium or aluminium alloy cathode may be scribed in the presence of a chlorine-containing gas.

The device could be fabricated with the cathode at the bottom, adjacent the substrate, and the anode on top. Then the anode could be patterned just as described above in relation to the cathode.

In more complex organic light-emitting devices laser scribing can allow for accurate shaping of the organic layers. An additional principle that may be employed makes use of the differences in absorption characteristics between different organic materials. By suitable choice of organic layers, one may be used to protect another during laser scribing. For example, if a YAG laser emitting at an infrared frequency is to be used it may be noted that PPV transmits infrared light, but PEDT/PSS absorbs strongly in the infrared. A PEDT/PSS layer may therefore provide some protection for an underlying PPV layer against the laser beam during scribing.

For example, (referring to figure 9) a multi-colour OLED may be fabricated by laser scribing/ablation patterning of the organic layer(s) as follows. The

substrate 1, with a semi-transparent bottom electrode 2 patterned in lines, is covered with a layer 3a of PEDT/PSS to act as a charge transporting and/or injecting layer. The PEDT/PSS layer is then coated with a blue-emitting electroluminescent polymer layer 4a (e.g. of a substituted polyfluorene). The polyfluorene is then laser scribed over all areas that are, in the final display, designed not to emit blue colour (figure 10). The laser ablation parameters are chosen such that the full polyfluorene thickness is ablated but not the full PEDT/PSS thickness, for example by using a laser wavelength which is in the absorption band of the blue-emitting polymer and by carefully choosing the laser pulse length and intensity. Thus the PEDT/PSS acts as both a charge transporting and/or injecting layer (in the finished device) and a buffer layer for laser ablation (during production).

The residual PEDT/PSS is then washed off, another PEDT/PSS layer (of which 3b is a residual portion) is spun and over it a green-emitting layer of PPV 4b is deposited. The green-emitting layer is then laser patterned in the same manner as the blue-emitting layer to leave green-emitting pixels on the display. The device is again cleaned of residual PEDT/PSS and a third PEDT/PSS layer (of which 3c is a residual portion) is spun and over it a red-emitting layer 4c of poly(2-methoxy-5(2'-ethyl)hexyloxy-phenylene-vinylene) ("MEH-PPV") is deposited. It in turn is laser patterned to leave red-emitting pixels (see figure 11). The device now has a pattern of blue-, green-, and red-emitting pixels. A cathode 5 is finally deposited and patterned to finish the multi-colour display (see figure 12; the patterning of the cathode is out of the plane of figure 12). The cathode is patterned in lines, possibly by one of the methods described above, so that the individual pixels can each be addressed in a conventional matrix format by means of one anode and one cathode line.

An OLED fabrication process using PEDT/PSS as a laser buffer/stopping layer is also useful when shaping the electrodes etc. using infra-red laser light, for example, 1064nm light from a YAG laser, which can efficiently scribe/ablate metals as well as conductive transparent inorganic oxides such as indium-tin-

oxide or tin-oxide but for which typical organic electroluminescent materials have less absorption.

Another alternative is to employ a protective layer of an electrically insulating material, between the top and bottom electrodes of a device, to act as a barrier during patterning. The protective layer is preferably of an inorganic material and preferably deposited and patterned on top of the bottom electrode. Then, when one of the electrodes is exposed to a patterning means such as a laser beam the protective layer could prevent the other electrode from being patterned. The protective layer could be of a material that is resistant to the patterning means and/or be sufficiently thick that its full thickness will not be removed during the patterning step and/or the rate of removal is much slower. If the patterning step is a laser scribing/ablation step then the protective layer could be of a material that absorbs at the wavelength of the laser light that is used.

Materials for the protective layer could include silicon nitride, silicon oxide or aluminium oxide. The protective layer may be especially advantageous in connection with such a patterning step because light of that wavelength could potentially scribe/ablate an electrode layer and/or an organic layer that can now be protected by the protective layer.

The protective layer could itself be a patterned layer, so that it provides protection to only selected regions of an underlying layer. For instance, in manufacturing a passive matrix organic light-emissive device the bottom electrode could be deposited and patterned in columns, then the protective insulating layer could be deposited, then an organic light-emissive layer (together with any other organic layers) could be deposited; and then the top electrode could be deposited and patterned by laser scribing in rows orthogonal to those of the bottom electrode. The protective layer could be patterned in (for example) a matrix of square-shaped regions to protect the bottom electrode during scribing of the top electrode. Another advantage of

this is that the edges of where the top electrode is removed (i.e. outer edges of the top electrode rows) can be slightly off-set from the active pixel area, i.e. the width of the square-shaped regions in the protective layer which define the active pixel areas is slightly smaller than the width of the row electrodes after patterning. This avoids or can at least reduce potential detrimental edge-effects.

The present invention may include any feature or combination of features disclosed herein either implicitly or explicitly or any generalisation thereof irrespective of whether it relates to the presently claimed invention. In view of the foregoing description it will be evident to a person skilled in the art that various modifications may be made within the scope of the invention. For example, it will be apparent to a person skilled in the art that other organic light-emitting materials could be used.

CLAIMS

1. A method for patterning an organic light-emitting device having an organic light-emitting layer underlying an electrode layer, the method comprising:
 - a first patterning step, in which the electrode layer is patterned by exposure to a laser beam so as to remove part of the depth of the electrode layer in the areas patterned by the laser beam; and
 - a second patterning step in which the remaining depth of the electrode layer is removed in the areas patterned during the first step, the second patterning step being of a type to which the organic layer is less sensitive than to that of the first patterning step.
2. A method as claimed in claim 1, wherein the first patterning step is of a type to which the organic layer is sensitive.
3. A method as claimed in claim 1 or 2, wherein the first patterning step is of an intensity sufficiently high to erode substantially material of the type comprised in the organic light-emitting layer.
4. A method as claimed in any preceding claim, wherein in the second step the electrode layer is patterned by a laser beam in an operation of a lower intensity than the first step.
5. A method as claimed in any preceding claim, wherein in the second step the electrode layer is patterned by etching.
6. A method as claimed in claim 5, wherein the etching is dry plasma etching.
7. A method as claimed in any preceding claim, wherein the electrode layer comprises an electrically conductive layer and a layer of protection material on the face of the conductive layer opposite the light-emitting layer.

8. A method as claimed in claim 7, wherein in the first step the full depth of the layer of protection material is removed.
9. A method as claimed in any of claims 1 to 6, wherein the electrode layer comprises an electrically conductive layer and a layer of laser absorbing material on the face of the conductive layer opposite the light-emitting layer.
10. A method as claimed in any of claims 7 to 9, wherein during the first patterning step the electrically conductive layer is not substantially patterned.
11. A method as claimed in any preceding claim, wherein the or each laser beam is applied as a pulsed laser beam.
12. A method as claimed in claim 11, wherein the or each laser beam is applied in pulses of less than 1ns.
13. A method as claimed in any preceding claim, wherein the electrode layer is transparent.
14. A method as claimed in any preceding claim, wherein the electrode layer is a cathode of the device and has at its face closest to the light-emitting layer a work function less than 3.5eV.
15. A method as claimed in any preceding claim, wherein the electrode layer is an anode of the device and has at its face closest to the light-emitting layer a work function greater than 4.5eV.
16. A method as claimed in any preceding claim, wherein the light-emitting layer is a light-emitting polymer layer.

17. A method as claimed in claim 16, wherein the light-emitting layer is a light-emitting conjugated polymer layer.

18. An organic light-emitting device manufactured by a method according to any preceding claim.

19. An organic light-emitting device as claimed in claim 18, wherein the electrode layer is a cathode layer of the device.

20. An organic light-emitting device as claimed in claim 18, wherein the electrode layer is an anode layer of the device.

21. A method for patterning an organic light-emitting device having an organic light-emitting layer underlying an electrode layer, the method comprising:

a first, higher intensity patterning step, in which the electrode layer is patterned by exposure to a relatively high intensity laser beam; and

a second, lower intensity patterning step, in which the electrode layer is rendered insulative in areas patterned during the first step.

22. A method for forming an organic light-emitting device on a substrate, comprising the steps of:

depositing a first layer of a conductive organic material on the substrate;

depositing a second layer of a light-emitting organic material on the first layer; and

patterning the second layer by exposing it to a laser beam of a frequency that is substantially absorbed by the conductive organic material and substantially absorbed by the light-emitting organic material.

23. A method as claimed in claim 22, wherein the light-emitting organic material is a polymer material.

24. A method as claimed in claim 22 or 23, wherein the light-emitting organic material is a conjugated material.

26. A method for forming an organic light-emitting device on a substrate, comprising the steps of:

depositing a first layer of a conductive material on the substrate;
depositing a second layer of a protective inorganic material on the first layer;

patterning the second layer by exposing it to a laser beam;
patterning the first layer by a dry etching process to which the second layer is insensitive;

depositing a third layer of a light-emitting organic material over the first and second layers; and

depositing a fourth layer of a conductive material over the third layer.

27. A method for patterning an organic light-emitting device substantially as herein described with reference to the accompanying drawings.

28. An organic light-emitting device substantially as herein described with reference to the accompanying drawings.

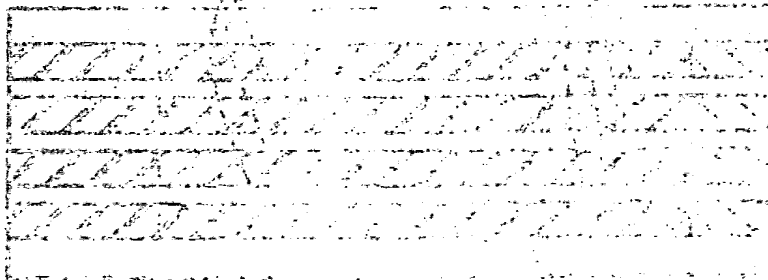


Fig.1.

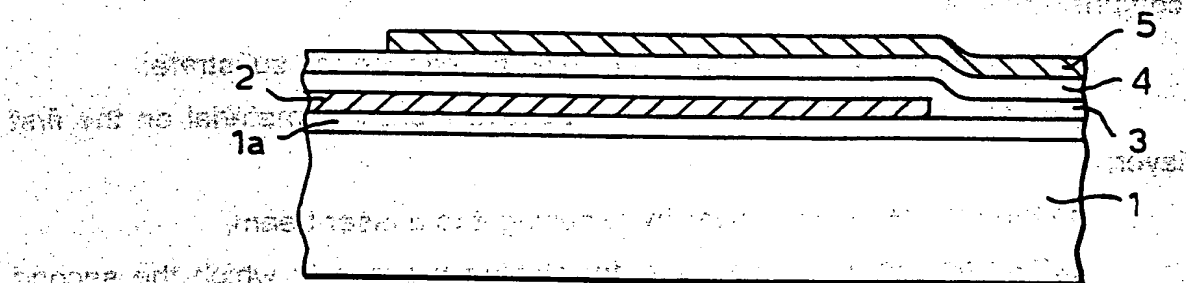


Fig.2.

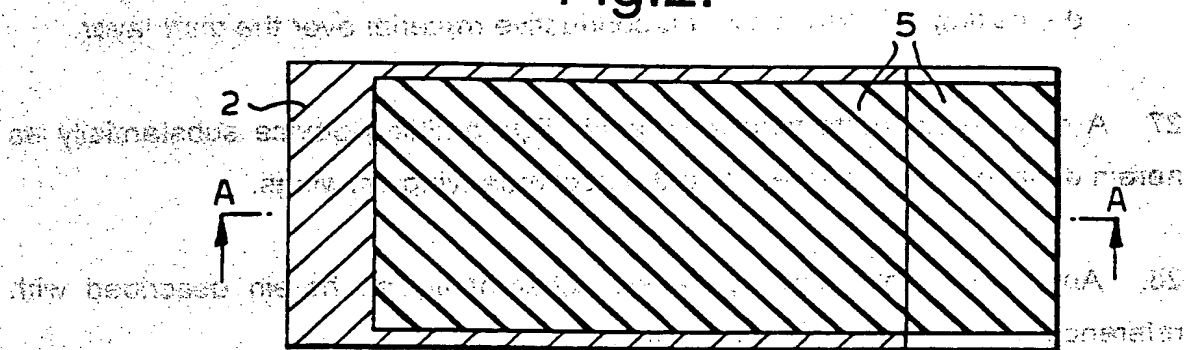
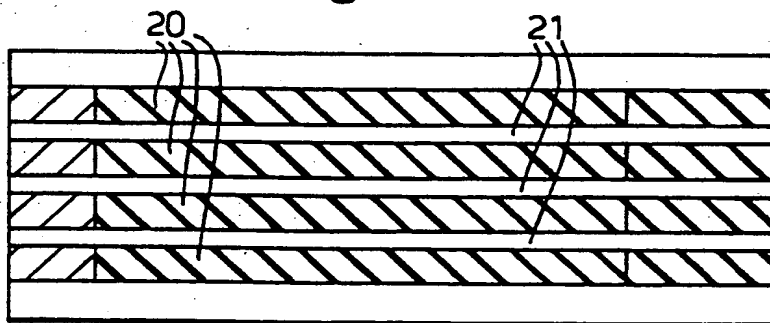


Fig.3.



2/3

Fig.4.

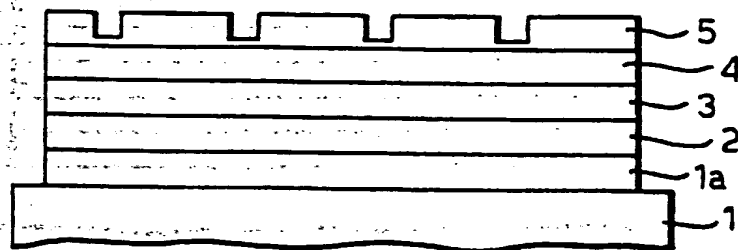


Fig.5.

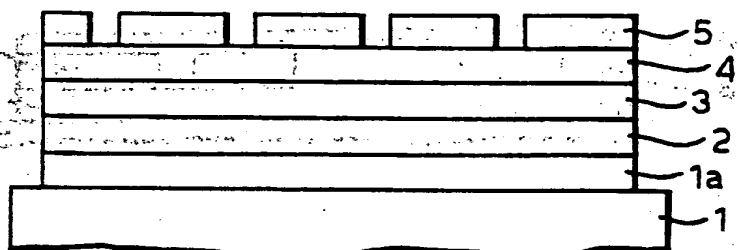


Fig.6.

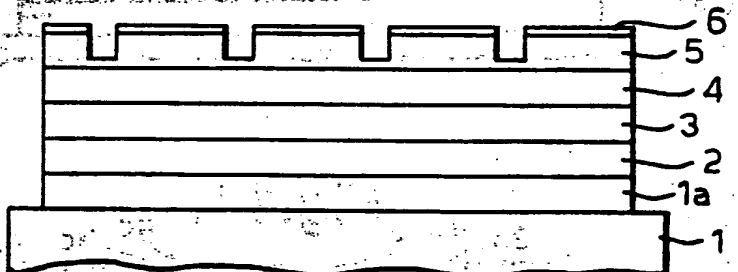
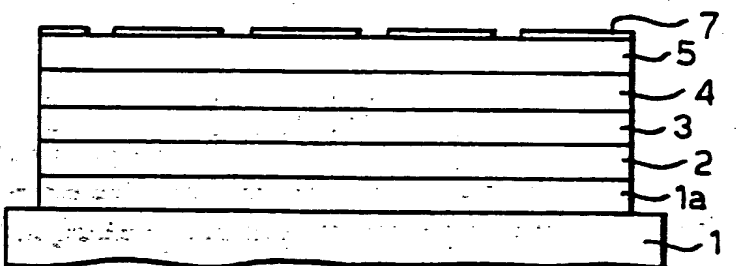


Fig.7.



3/3

Fig.8.

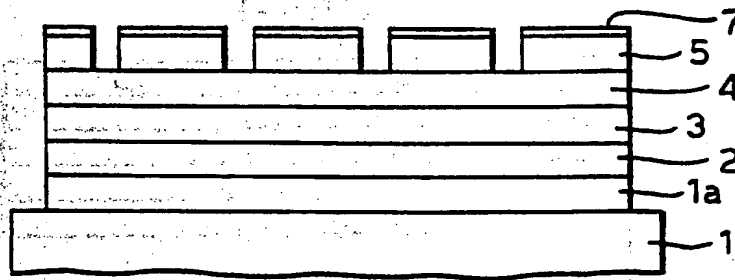


Fig.9.

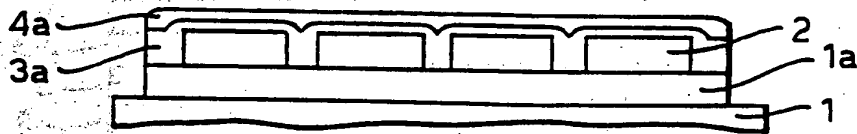


Fig.10.

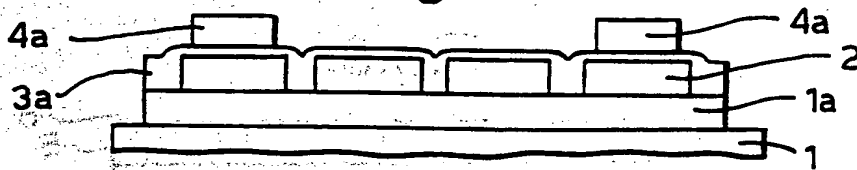


Fig.11.

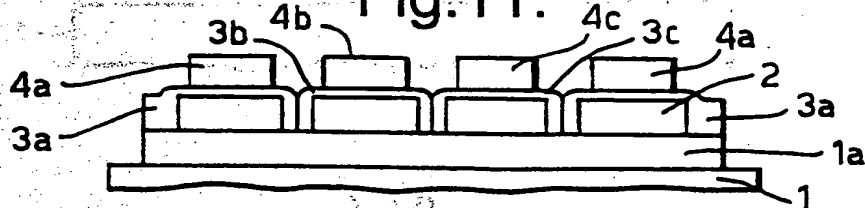
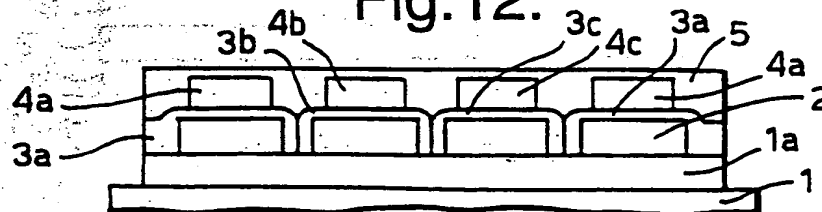


Fig.12.



INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 98/01265

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 H01L51/20 H01L27/15

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y A	EP 0 758 192 A (PIONEER ELECTRONIC CORP) 12 February 1997 cited in the application see the whole document	1-3, 5, 6, 9 11, 14, 18, 19, 21, 22, 26-28
Y A	WO 90 09730 A (AUTODISPLAY AS) 23 August 1990 see claims 1, 7, 13	1-3, 5, 6, 9 11, 13, 15, 21, 22, 26-28
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

3 August 1998

Date of mailing of the international search report

09/09/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+31-70) 340-3016

Authorized officer

De Laere, A

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 98/01265

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>NOACH S ET AL: "MICROFABRICATION OF AN ELECTROLUMINESCENT POLYMER LIGHT-EMITTING DIODE PIXEL ARRAY" APPLIED PHYSICS LETTERS, vol. 69, no. 24, 9 December 1996, pages 3650-3652, XP000644107 cited in the application see the whole document</p> <p>-----</p>	<p>1-3, 11, 13-28</p>

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 98/01265

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
EP 0758192	A	12-02-1997	JP	9050888 A	18-02-1997
WO 9009730	A	23-08-1990	AU	5097190 A	05-09-1990

REF ID: A61504	A 041504	16	0001 00 00	A 041504 00
----------------	----------	----	------------	-------------